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(54) Cosmetic screening composition

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(57) A UV screening composition contains (i) at least one UV screen, (ii) an aqueous dispersion of particles of a water-insoluble polymer comprising a) an ionic polymer, forming a core, containing ionizable acid groups which make the core capable of being swollen by at least partial neutralization with a volatile base and b) a polymer forming a sheath at least partially encapsulating the core and permeable to the volatile base, the sheath having a glass transition temperature below 50°C and the particles being film-forming, which is obtained by a process of block polymerization in emulsion and (iii) a cosmetic base. "Ropaque OP42" can be used as the water insoluble polymer. The effect of the polymer is to increase the protection index of the screening composition. The composition is e.g. in the form of a sunscreen milk or cream, salve, gel or aerosol.

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SPECIFICATION

Cosmetic screening composition

5 The present invention relates to a cosmetic composition screening ultraviolet radiations, containing a UV screen and a polymer obtained by block polymerization in emulsion, the effect of which is to increase the protection index of the said screening composition, and the use of the said composition to protect the human epidermis against ultraviolet radiations.

UV 5 the

It is known that light radiations of wavelengths between 280 and 320 nm, known by the name of UV.B, 10 produce erythemas and cutaneous burns whose severity increases rapidly with the duration of exposure.

As a result, agents which screen these radiations and whose effectiveness is expressed by a suppro-

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As a result, agents which screen these radiations and whose effectiveness is expressed by a sun protection factor, which is conventionally called a protection index or PI, are added to sunscreen preparations.

Irradiation time required to reach the erythematogenic threshold with a UV screen

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PI = Irradiation time required to reach the erythematogenic threshold without a UV screen

It is known, furthermore, that in some cases the agents which screen the UV.B rays can give rise to adverse secondary effects, and that it is in the cosmetologist's interest to obtain the required protection index with the lowest possible quantity of screening agent in the composition.

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Moreover, it is difficult to obtain, using means known hitherto, a cosmetic screening composition which, in addition to a high protection index, does not allow a whitish film, hardly appreciated by the 25 users, to remain on the skin after an application, which is not sticky to the touch and which has good chemical and photochemical stability.

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Surprisingly, the applicant has found that by adding to a cosmetically acceptable base containing at least one oil-soluble and/or water-soluble agent screening the ultraviolet radiations, an aqueous dispersion of particles of a water-insoluble polymer defined hereinafter, a cosmetic composition is obtained 30 which screens the UV.B rays, and which has the combination of the above required characteristics and more especially an increased protection index, which advantageously enables the content of the screening agent in the earlier compositions to be reduced.

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The subject of the present invention is consequently a cosmetic composition screening the UV rays, containing, in a cosmetically acceptable base, at least one oil-soluble and/or water-soluble agent screen-35 ing the ultraviolet radiations and at least one aqueous dispersion of particles of a water-insoluble polymer, comprising:

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a) an ionic polymer forming a core, containing ionizable acid groups which make the core capable of being swollen by at least partial neutralization with a volatile base and,

b) a polymer forming a sheath at least partly encapsulating the core and permeable to the volatile 40 base, the outer sheath having a glass transition temperature below 50°C and the particles being film forming, the said aqueous dispersion of polymer being obtained by the process of block polymerization in emulsion described in Patent Application EP 73,529, where it is employed especially as a thickening agent for aqueous coating compositions.

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Another subject of the present invention is a process for protecting the human epidermis against the 45 UV rays, consisting in applying on the skin an effective quantity of the cosmetic screening composition defined above.

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The cosmetic screening composition according to the invention contains at least one aqueous dispersion of an acrylic heteropolymer described in the abovementioned Patent Application EP 73,529 and more particularly an aqueous dispersion of a water-insoluble acrylic heteropolymer prepared according 50 to the process of block polymerization in emulsion, described in the said application and such that the sheath polymer has a glass transition temperature of -40°C to +23°C and encapsulates the core polymer to an extent of over 50% and preferably over 85%, and that the volatile base required to swell the core is in a sufficient quantity to obtain a pH of at least 6 and preferably 9-10.

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The preferred monomers used in the core polymer are arcylic and/or methacrylic acid in a proportion 55 of at least 15% by weight and a polyunsaturated crosslinking monomer in a proportion of 0.1% to 3% relative to the total weight of the core monomers, where the acrylic and/or methacrylic acid present in the sheath monomer must not exceed 10% of the total weight of the sheath monomer and must be less than one third of its proportion in the core monomer. The size of the core/sheath particles before swelling by neutralization is between 0.07 and 4.5 microns, preferably between 0.1 and 3.5 and advanta-

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60 geously between 0.2 and 2 microns.

The core polymer preferably comprises, as a polyunsaturated crosslinking monomer, ethylene glycol di(meth)-acrylate, allyl (meth)acrylate, 1,3-butanediol di(meth)-acrylate, diethylene glycol di(meth)acrylate, trimethylolpropane trimethacrylate or divinylbenzene.

Preferably, the polymer sold under the name "Ronague OP 42" by the company Rohn and Haas is

5	The polymer is present in the cosmetic screening composition according to the invention in a proportion of 0.1% to 10% by weight of active substance relative to the total weight of the composition, and preferably in a proportion of 0.5% to 5% by weight, and the agents screening the ultraviolet radiations are present at a total concentration of 1% to 20% by weight and preferably from 2 to 15% by weight relative to the total weight of the composition. Among the known screens which can be used in the cosmetic screening composition according to the invention there may be mentioned the UV-A and UV-B screens such as, for example: - benzylidenecamphors such as:	5
0	- 3-benzylidene-d,l-camphor	10
5	- sulphonamide derivatives of 3-benzylidenecamphor which are described and prepared in Belgian Patent 897,241 of the applicant - p-benzylidenecamphor derivatives such as the 3-p-oxy-benzylidene-2-bornanones described and prepared in Belgian Patent No. 877,596 of the applicant, and other benzylidenecamphor derivatives such as those described and prepared in French Patents 2,199,971, 2,236,515 and 2,282,426 of the applicant and more particularly 4;-ob(2-oxo-3-bornylidene)methyl]phenyltrimethylammonium methyl sulphate and salts	15
20	of 4-(2-oxo-3-bornylidenemethyl)benzenesulphonic acid and 2-methyl-5-(2-oxo-3-bornylidenemethyl)benzenesulphonic acid, - 3-cinnamylidenecamphor - 1,4-dicamphormethylidenebenzenes and camphormethylidenecinnamates described and prepared in	20
25	Belgian Patent 897,051 of the applicant; - p-aminobenzoic acid, its esters and derivatives such as: - ethyl p-aminobenzoate, sold under the trademark Benzocaine - isopropyl p-aminobenzoate - isobutyl p-aminobenzoate, sold under the trademark Cycloform	25
30	- ethyl N-(2-hydroxypropyl)-p-aminobenzoate and ethyl N,N-bis(2-hydroxypropyl)-p-aminobenzoate, which are sold under the trademark Amerscreen P	30
35	 ethyl 4-(dimethylamino)benzoate amyl 4-(dimethylamino)benzoate or "Padimate" according to the common international nomenclature, sold under the trademark Escalol 506 2-ethylhexyl 4-(dimethylamino)benzoate, sold under the trademark Escalol 507 3,3,5-trimethylcyclohexyl 2-acetamidobenzoate; 	3!
10	- cinnamates such as:	40
45	 2-ethylhexyl p-methoxycinnamate, sold under the trademark Parsol MCX and Neó Heliopan AV amyl and isoamyl p-methoxycinnamate, sold under the trademark Néo Héliopan E 1000 propyl p-methoxycinnamate 	45
50	 cyclohexyl p-methoxycinnamate 2-ethoxyethyl p-methoxycinnamate or 'Cinoxate' according to the common international nomenclature, sold under the trademark Giv-Tan F potassium cinnamate 	50
55	 salts of p-methoxycinnamic acid, such as the sodium, potassium and diethanolamine salts; salicylates such as: 	55
60	sol A	60
	- other compounds such as:	e.

	athud wasanata	
	 ethyl urocanate the trioleate of 3,4-dihydroxy-5-[(3,4,5-trihydroxybenzoyl)oxy]benzoic acid, sold under the trademark 	
	Solprotex 1	
	- sodium 3,4-dimethoxyphenylglyoxylate	
5		5
5	- benzophenone derivatives such as:	-
	- 2-hydroxy-4-methoxybenzophenone or "oxybenzone", sold under the trademarks Spectra-Sorb UV 9,	
	Uvinul M 40 and Eusolex 4360	
	-2,2'-dihydroxy-4-methoxybenzophenone or "dioxybenzone", sold under the trademark Cyasorb UV 24	
10	-2,4-dihydroxybenzophenone, sold under the trademark Uvinul 400	10
	-2,2',4,4'-tetrahydroxybenzophenone, sold under the trademark Uvinul D 50	
	- 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, sold under the trademark Uvinul D 49	
•	- 2-hydroxy-4-methoxy-4'-methylbenzophenone or 'mexenone', sold under the trademark Uvistat 2211	
	- 2-hydroxy-4-(n-octyloxy)benzophenone or "octobenzone", sold under the trademark Cyasorb UV 531	
15	- 4-phenylbenzophenone, sold under the trademark Eusolex 3490	15
	- 2-ethylhexyl 2-(4-phenylbenzoyl)benzoate, sold under the trademark Eusolex 3573	
	- 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid and its sodium salt or "Sulisobenzone" and "sodium Sulisobenzone", sold under the trademark Uvinul MS 40;	
	- dibenzoylmethane derivatives such as:	
20	A L. M. A.	20
20	- 4-tert-butyl-4'-methoxy-dibenzoylmethane, sold under the trademark Parsol 1789	20
	dianisoylmethane, sold under the trademark Parsol DAM;	
	- certain benzotriazole derivatives such as:	
	- 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, sold under the trademark Tinuvin P	
25	a tark in the second of the third through the second conduction and a second Consistent Conductive Cards.	25
	The above list of sunscreens is obviously not restrictive.	
	At least one of the following compounds is preferably employed as an agent absorbing the UV rays:	
	- 2-ethylhexyl p-(dimethylamino)benzoate (Escalol 507)	
	- 2-ethylhexyl p-methoxycinnamate (Parsol MCX)	
30		30
	- 3-(4'-methylbenzylidene)-d,l-camphor (Eusolex 6300)	
	amyl 4-(dimethylamino)benzoate (Escalol 506)	
	 homomenthyl salicylate (Filtrasol A) 2-hydroxy-4-methoxybenzophenone (Uvinul M 40 - Spectra-Sorb UV 9) 	
35		35
55	- N-(2-ethylhexyl)-3-benzylidene-10-camphor sulphonamide, optionally in combination with one of the	-
	following compounds:	
	tert-butyl-4-methoxy-4'-dibenzoylmethane (Parsol 1789)	
	- 4-isopropyldibenzoylmethane (Eusolex 8020)	
40	- α-(2-oxo-3-bornylidene)toluene-4-sulphonic acid and its salts	40
	- α-(2-oxo-3-bornylidene)-p-xylene-2-sulphonic acid	
	- 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid	
	- 4-[(2-oxo-3-bornylidene)methyl]phenyltrimethylammonium methyl sulphate	
	- 1,4-di[sulphocamphorylmethylidene]benzene acid, and	45
45	 2-phenylbenzimidazole-5-sulphonic acid. Besides the polymer obtained by block polymerization in emulsion and described in EP-A-0,073,529 	45
	and the agents absorbing the ultraviolet radiations, the cosmetic screening composition according to the	
	invention can contain cosmetic adjuvants usually employed in a composition of this type.	
	Among the principal adjuvants which can be present in a composition of this kind, there may be men-	
50) tioned solvents such as water, lower monoalcohols or polyalcohols containing from 1 to 6 carbon atoms,	50
	or mixtures thereof; there may also be mentioned fatty substances such as oils or mineral, animal or	
	plant waxes, fatty acids, fatty acid esters such as triglycerides of fatty acids containing from 6 to 12 car-	
	bon atoms, fatty alcohols and oxyethylenated fatty alcohols.	
	The mono- or polyalcohols which are more especially preferred are chosen from ethanol, isopropanol,	
55	propylene glycol, glycerol and sorbitol.	55
	As fatty substances, among the mineral oils there may be mentioned paraffin oil; among the animal oils, whale, seal, alosa, halibut liver, cod, tuna, turtle, tallow neat's-foot, horse's hoof, sheep's foot, mink,	
	otter, marmot oils and the like; among the plant oils, almond, peanut, wheatgerm, olive, maize germ,	
	jojoba, sesame, sunflower, palm, nut oils, and similar oils.	
60		60
	stearic acids and the fatty esters which are solid at 25°C.	
	Vaseline, paraffin, lanolin, hydrogenated lanolin, acetylated lanolin and silicone oil can also be men-	
	tioned as fatty substances.	
	Among the wayon there may be mentioned Sinel way lanelin way heesway candelilla way micro-	

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which are solid at 25°C, sucroglycerides, and Ca, Mg, Zr and Al oleates, myristates, linoleates and stearates.

Among the fatty alcohols there may be mentioned lauryl, cetyl, myristyl, stearyl, palmityl and oleyl alcohols, and among the polyoxyethylenated fatty alcohols, lauryl, cetyl, stearyl and oleyl alcohols containing from 2 to 20 moles of ethylene oxide.

The cosmetic composition can also contain emulsifiers which can be nonionic, anionic, cationic or amphoteric.

It may also be useful to use thickeners such as cellulose derivatives, polyacrylic acid derivatives, or guar or carob gums.

The cosmetic composition according to the invention can also contain adjuvants usually employed in cosmetics and especially hydrating products, emollients, dyes, preserving agents and perfumes.

The cosmetic screening composition according to the invention may be presented in the form of an emulsion (cream or milk), a salve, a gel, or be packaged as an aerosol, and in general, in any of the usual forms of the antiactinic cosmetic compositions.

The invention will be illustrated better with the aid of the following restrictive examples:

Example 1 EMULSION (sunscreen cream).

27770	Polymer sold in aqueous emulsion at a		
20	concentration of 40% AS under the name Ropaque OP 42 by the company Rohm & Haas	2.0 g AS	20
	2-ethylhexyl 4-(dimethylamino)benzoate	2.5 g AS	
25	2-hydroxy-4-methoxybenzophenone	1.0 g AS	25
	Mixture of glycerol mono- and distearate, not self-emulsifiable, sold under the name of Geleol Copeaux by the company Gattefosse	2.0 g AS	
20	Mixture of cetylstearyl alcohol and of cetyl- stearyl alcohol oxyethylenated with 33 moles of ethylene oxide, sold under the name "Sinnowax		30
25	AO" by the company Henkel	7.0 g AS	35
25 30 35	Cetyl alcohol	1.5 g AS	,
	Silicone oil	1.5 g AS	
40	Paraffin oil	15.0 g	40
	Glycerine	20.0 g	
45	Perfume preserving agent q.s.		45
45	Water q.s.	100.0 g	45

It is found that the emulsion of this example, containing the polymer Ropaque OP 42, has a sun protection index equal to 6.5, whereas that of the emulsion which contains only the UV screen consisting of 2-50 ethylhexyl 4-(dimethylamino)benzoate and 2-hydroxy-4-methoxybenzophenone is equal to 4.7.

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	nple 2 ILSION (sunscreen milk) Parsol MCX (2-ethylhexyl p	o-methoxycinnamate	4.0 g	
5	Ropaque OP 42		3.0 g AS	5
	Stearyl alcohol		2.7 g	
	Isopropyl palmitate		5.0 g	10
10	Cetylstearyl alcohol contain of ethylene oxide	ning 33 moles	2.7 g	10
45	Preserving agent	q.s.		15
15	Perfume	q.s.		15
	Demineralized water	q.s.	100 g	
	nple 3 ILSION (sunscreen cream)			20
	Eusolex 6300 (3-(4'-methylbenzylidene)-d,l-camphor		4.0 g	
25	Ropaque OP 42		3.5 g AS	25
	Sipol wax		7.0 g	
30	Glycerol monostearate		2.0 g	30
	Paraffin oil		15.0 g	
0.5	Silicone oil		1.5 g	35
35	Cetyl alcohol		1.5 g	33
	Glycerine		10.0 g	
40	Perfume	q.s.		40
	Preserving agent(s)	q.s.	,	
45	Dye(s)	q.s.		45
40	Water	q.s.	100 g	40

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Exam; EMUL	o <i>le 4</i> SION (sunscreen cream) 4-[(2-oxo-3-bornylidene)m	nethyl]phenyltrimethyl-			
5	ammonium methyl sulpha Examples 1 or 2 of French	ate prepared according to	1.0 g	5	
	Benzylidenecamphor		2.0 g		
	Ropaque OP 42		2.5 g		
0	Cetyl alcohol		1.2 g	10	
	Self-emulsifiable glycerol monostearate		7.4 g		
5	Sorbitan monostearate po		2.7 g	15	
	Lanolin		4.0 g		
0	Paraffin oil		30.0 g	20	
	Perfume	q.s.			
	Preserving agent(s)	q.s.			
5	Dye(s)	q.s.		25	
	Water	q.s.	100 g		
0 Examp EMUL	S/ON (sunscreen cream)			30	
	4-tert-butyl-4'-methoxydibenzoylmethane (parsol 1789)		0.5 g		
5	2-Ethylhexyl p-methoxycir	nnamate (Parsol MCX)	3.0 g	35	
	Ropaque OP 42	3.0 g AS			
0	Mixture of cetylstearyl alc alcohol oxyethylenated wi ene oxide, sold under the		40		
	the company Henkel	8.0 g			
5	Mixture of nonemulsifiable glycerol mono- and distearate, sold under the name Geleol Copeaux by the company Gattefosse			45	
			2.0 g		
Cetyl alcohol 0 Paraffin oil		2.0 g	50		
		15.0 g	50		
	Glycerine		18.0 g		
5	Propylene glycol		2.0 g	55	
	Perfume, preserving agen	t q.s.			
	Water	q.s.	100 g		

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Example	9 6			
EMULSI	ON (sunscreen milk) Homomenthyl salicylate		6.0 g	
5	2-Ethylhexyl p-(dimethylamino (Escalol 507))benzoate	1.0 g	5
	Ropaque OP 42		2.5 g AS	
0	Stearyl alcohol		2.7 g	10
	Isopropyl palmitate		5.0 g	
5	Cetylstearyl alcohol containing ethylene oxide	33 moles of	2.7 g	15
	Perfume, preserving agent	q.s.		
0	Water	q.s.	100 g	20
Exampl EMULS	le 7 FON (sunscreen cream) N-(2-ethylhexyl)-4-(3'-methylic benzenesulphonamide	lenecamphor)-	0.5 g	25
	5-Methyl-2-phenylbenzoxazole	e (Witisol)	0.5 g	
10	5-(3,3-Dimethyl-2-norbornylide 2-one (Prosolal 59)	ene)-3-penten-	3.0 g	30
	Ropaque OP 42		3.5 g AS	
5	Triglycerides of caprylic/caprid sold under the name Miglyol a Dynamit Nobel		20.0 g	35
0	Mixture of cetylstearyl alcoho aryl alcohol containing 33 mo oxide, sold under the name "t the company Henkel	les of ethylene	9.0 g	40
	Cetyl alcohol		3.0 g	
5	70% sorbitol		8.0 g	45
	Preserving agent, perfume	q.s.		
50	Water	q.s.	100 g	50
CLAIMS	s			
1. A 55 at least mer ob ionic po	cosmetic composition for screen one UV screen in combination w tained by a process of block polyr olymer, containing ionizable acid	ith an aqueous dispersion of merization in emulsion, each groups such that the core is c	in a cosmetically acceptable base particles of a water-insoluble poly- particle comprising a) as a core, an apable of being swollen by at least	
polyme the par	neutralization with a volatile base or permeable to the volatile base, to ticles being film forming.	the sheath having a glass tran	nsition temperature of 50°C or less,	60

2. A cosmetic screening composition according to Claim 1 comprising an aqueous dispersion of a water-insoluble acrylic heteropolymer in which the sheath polymer has a glass transition temperature of from -40°C to 23°C and encapsulates the core polymer to an extent of over 50%, the volatile base re-

quired to swell the core being present in sufficient quantity to obtain a pH of at least 6.

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obtained from a mixture of monomers comprising at least 15% of acrylic and/or methacrylic acid by weight based on the total weight of the core monomers and 0.1 to 3% by weight of a poly-unsaturated crosslinking monomer, and wherein sheath polymer is obtained from a mixture of monomers comprising acrylic and/or methacrylic acid in an amount not exceeding 10% by weight based on the total weight of the sheath monomers and which is less than one third of the proportion of acrylic and/or methacrylic acid in the core monomers, the size of the particles before swelling by neutralization being from 0.07 to 4.5 μm.

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- 4. A cosmetic screening composition according to any one of Claims 1 to 3, comprising the polymer "Ropaque OP 42" as an aqueous dispersion of particles.
- ₀ 5. A cosmetic screening composition according to any one of Claims 1 to 4, wherein the polymer is present at from 0.1 to 10% by weight based on the total weight of the composition.

from 0.5

- 6. A cosmetic screening composition according to Claim 5, wherein the polymer is present at from 0.5 to 5% by weight.
- 7. A cosmetic screening composition according to any one of Claims 1 to 5, wherein the UV screens 15 are present, in total, at from 1 to 20% by weight based on the total weight of the composition.

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- 8. A cosmetic screening composition according to Claim 7 wherein the UV screens are present, in total, at from 2 to 15% by weight.
- 9. A cosmetic screening composition according to any preceding claim wherein each UV screen is chosen from benzylidenecamphors, p-aminobenzoic acid, its esters and derivatives, anthranilates, cinna-20 mates, salicylates, benzoxazole derivatives, 5-(3,3-dimethyl-2-norbornylidene)-3-penten-2-one, ethyl urocanate, the trioleate of 3,4-dihydroxy-5-[(3,4,5-trihydroxybenzoyl)oxy] benzoic acid, sodium 3,4-dimethoxyphenylglyoxylate, 2-phenylbenzimidazole-5-sulphonic acid and its salts, benzophenone derivatives, dibenzoylmethane derivatives and benzotriazole derivatives.

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10. A cosmetic screening composition according to Claim 9 comprising, as UV screen, at least one of 25 the following compounds: 2-ethylhexyl p-(dimethylamino) benzoate, 2-ethylhexyl p-methoxycinnamate, 3-benzylidene-d,l-camphor, 3-(4'-methylbenzylidene)-d,l-camphor, amyl 4-(dimethylamino)benzoate, homomenthyl salicylate, 2-hydroxy-4-methoxybenzophenone, N-(2-ethylhexyl)-4, (3'-methylidenecamphor)benzene sulphonamide, and N-(2-ethylhexyl)-3-benzylidene-10-camphor sulphonamide.

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11. A cosmetic screening composition according to Claim 10 further comprising one of the following 30 compounds: tert-butyl-4-methoxy-4'-dibenzoylmethane, 4-isopropyldibenzoylmethane, α-(2-οxο-3-bornylidene)toluene-4-sulphonic acid and its salts, α-(2-οxο-3-bornylidene)-p-xylene-2-sulphonic acid, 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid, 4-[(2-οxο-3-bornylidene)methyl]-phenyltrimethylammonium methyl sulphate, 1,4-di[sulphocamphorylmethylidene]benzene acid and 2-phenylbenzimidazole-5-sulphonic acid.

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35 12. A cosmetic screening composition according to any preceding claim further comprising one or more usual cosmetic adjuvants. 35

13. A cosmetic screening composition according to Claim 12 wherein the adjuvants are chosen from solvents, fatty substances, thickeners, emollients, hydrating products, dyes, preserving agents, perfumes and propellants.

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- 10 14. A cosmetic screening composition according to any preceding claim presented in the form of an emulsion, a salve, a gel, or packaged as an aerosol.
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- 15. A cosmetic screening composition according to Claim 14 presented as a cream or milk.
- 16. A cosmetic screening composition according to Claim 1 and substantially as hereinbefore described with reference to any one of the Examples.

17. A process for protecting human epidermis against the UV rays comprising applying, to the skin,

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- an effective quantity of a cosmetic screening composition according to any preceding claim.

 18. A process according to Claim 17 substantially as hereinbefore described.